RESEARCH CAPABILITIES: COMBUSTION – DERIVED TRACE METALS AND PARTICULATE MATTER

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CURRENT RESEARCH AREAS

Particulate Matter (PM 2.5) and Ash

- *monitor for PM 2.5 composition*
- *single particle composition*
- *pdf for particle morphology*
- *particle coalescence modeling*
- *ash formation under elevated P, P_{O2}*

CO2 Capture using supported amine dry sorbents

Trace Metals

- *As, Se, Cr emissions prediction based on partitioning*
- *Metal speciation measurement, modeling*
- *Hg emissions – experiments, modeling*

Mechanisms - PM 2.5 Health Effects?

Concentration of ambient PM 2.5 linked to human health

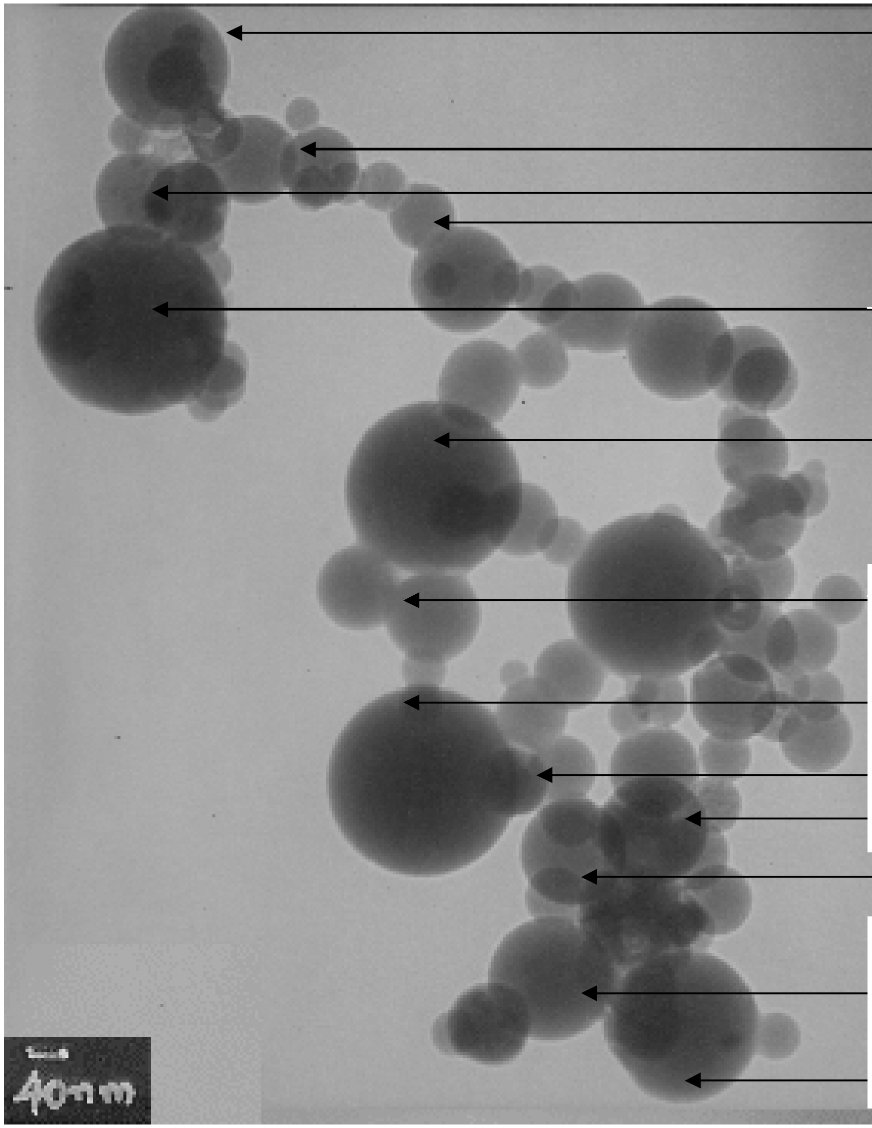
No association with coarse bulk composition

Little known about particle - to - particle variations

Little known about responsible particles

- ***trace metal surface coatings?***
- ***secondary particles?***
- ***need to predict surface area distributions for condensation***
- ***morphology determining; no data on <u>distributions</u> in literature***

Ambient PM Heterogeneous



Si - 74%, Mn 6%, Fe 7%

} Si - 67%, Mn 5%, Fe 15%

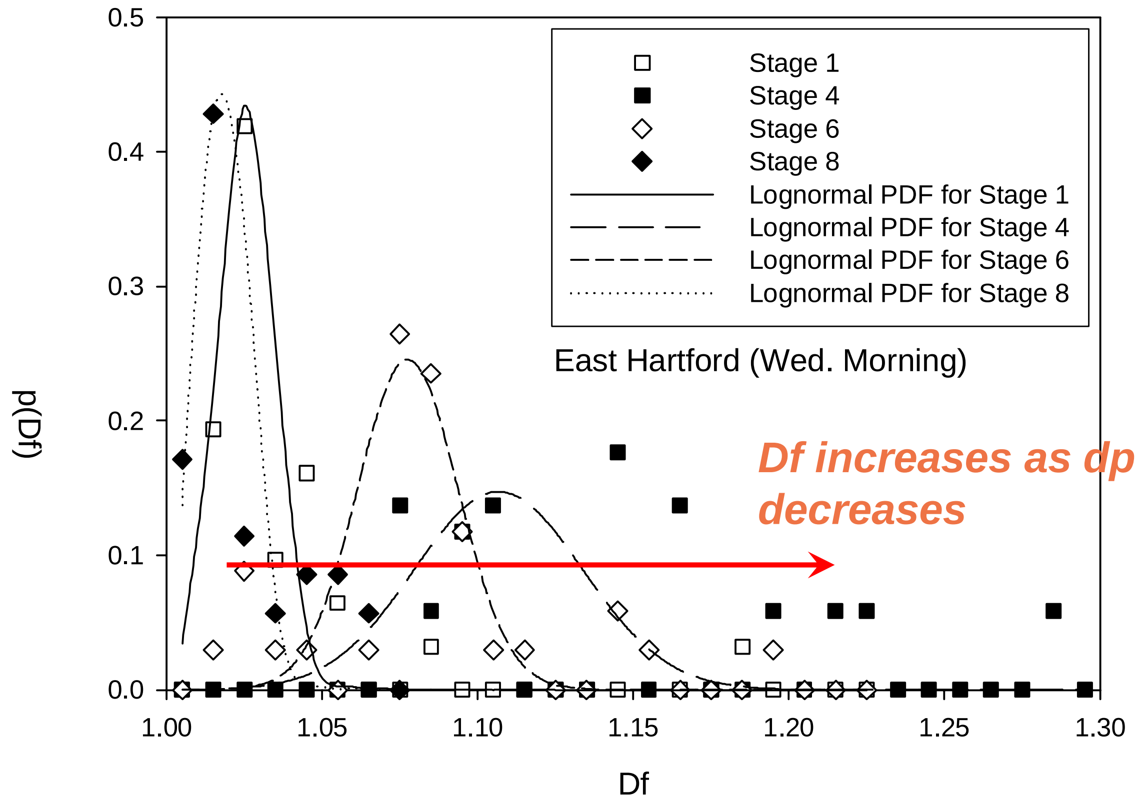
Si - 59%, Mn 4%, Fe 13%

Si - 66%, Mn 5%, Fe 12%

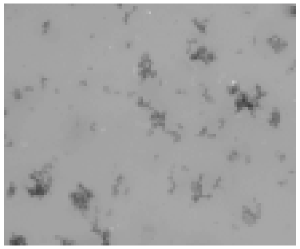
Si - 71%, Mn 6%, Fe 8%

Ambient particles: > ½ of fractals inorganic

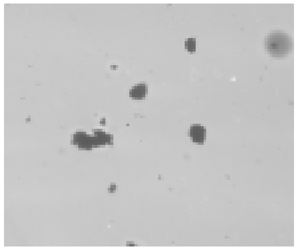
East Hartford CT – Morphology pdf



Stage 4 d = 0.15 um



Stage 8 d = 2.1 um



Log normal distribution

Weekday rush hour

Preliminary analysis: differences in Df (surface area) with day of week – effects on condensation?

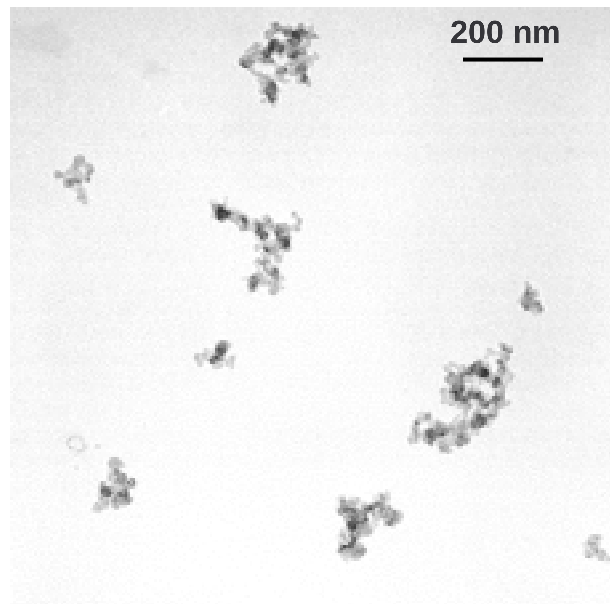
Similar to Coal-derived Submicron Ash

Mass fractal scaling: $N = k_g (r_g/d_p)^{Df}$

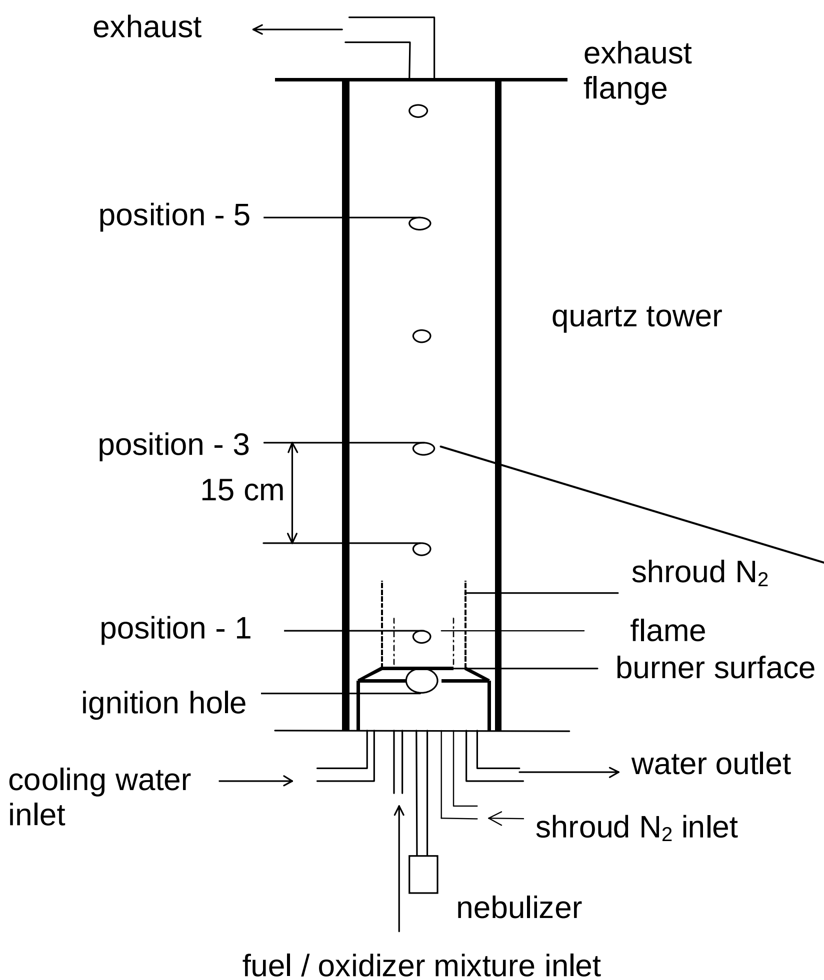
Samples collected from 1 MWth combustor

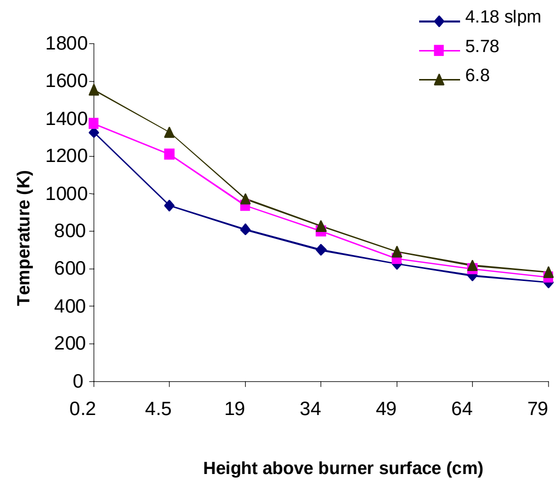
- *T = 1773 K, 1873 K*
- *coal type*
- *ESP inlet, outlet*

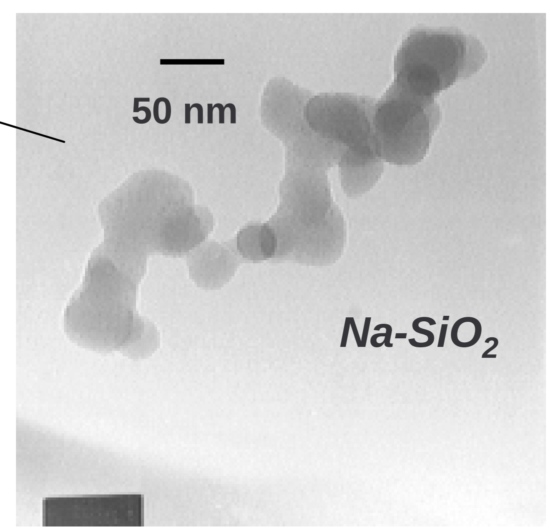
Cascade impactor used for size segregation from 0.016 - 0.46 μm



Experimental System to Study Structure







(thermophoretic sampling)

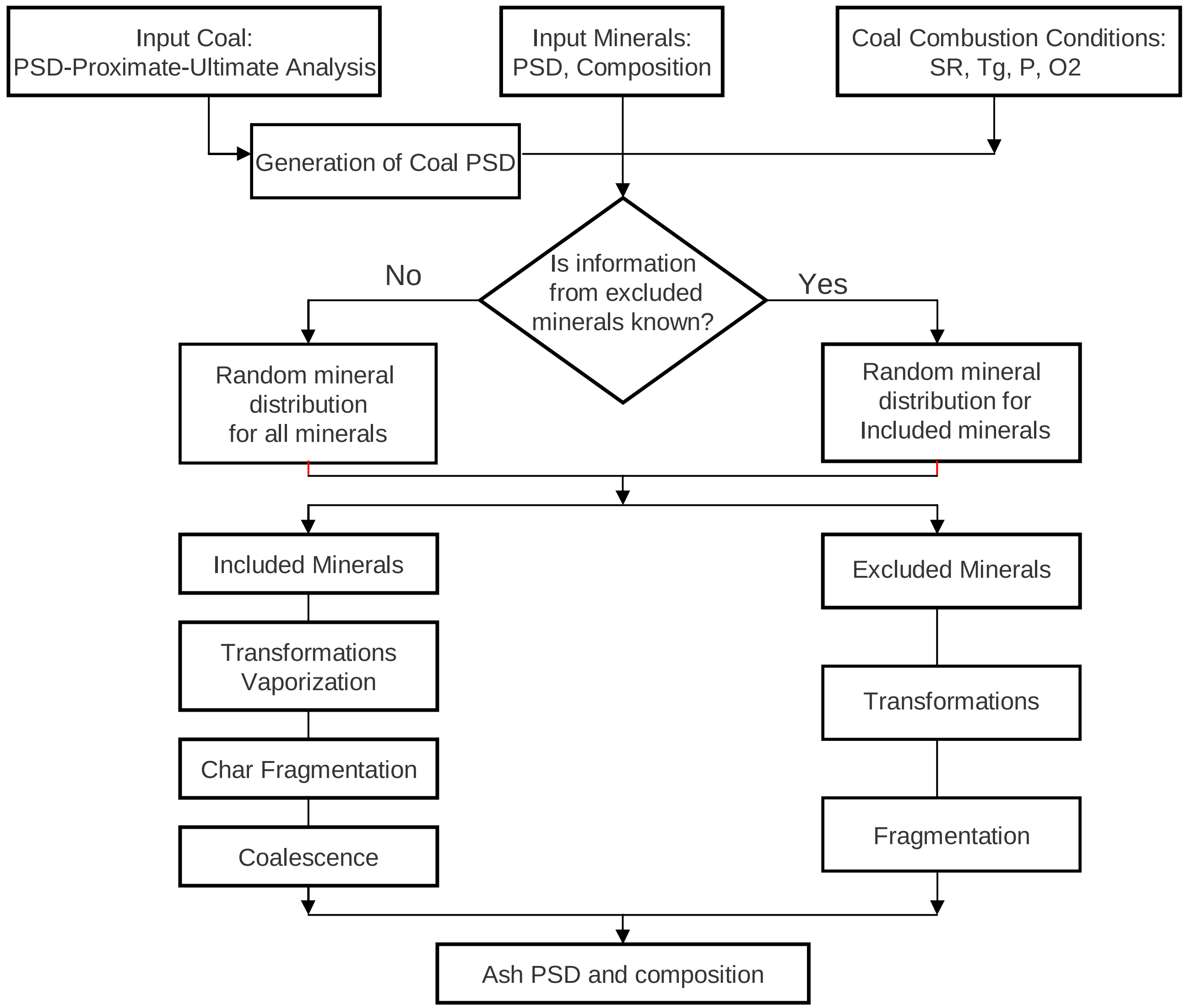
SiO_2

MgO

SiO_2-Na

SiO_2-Mg

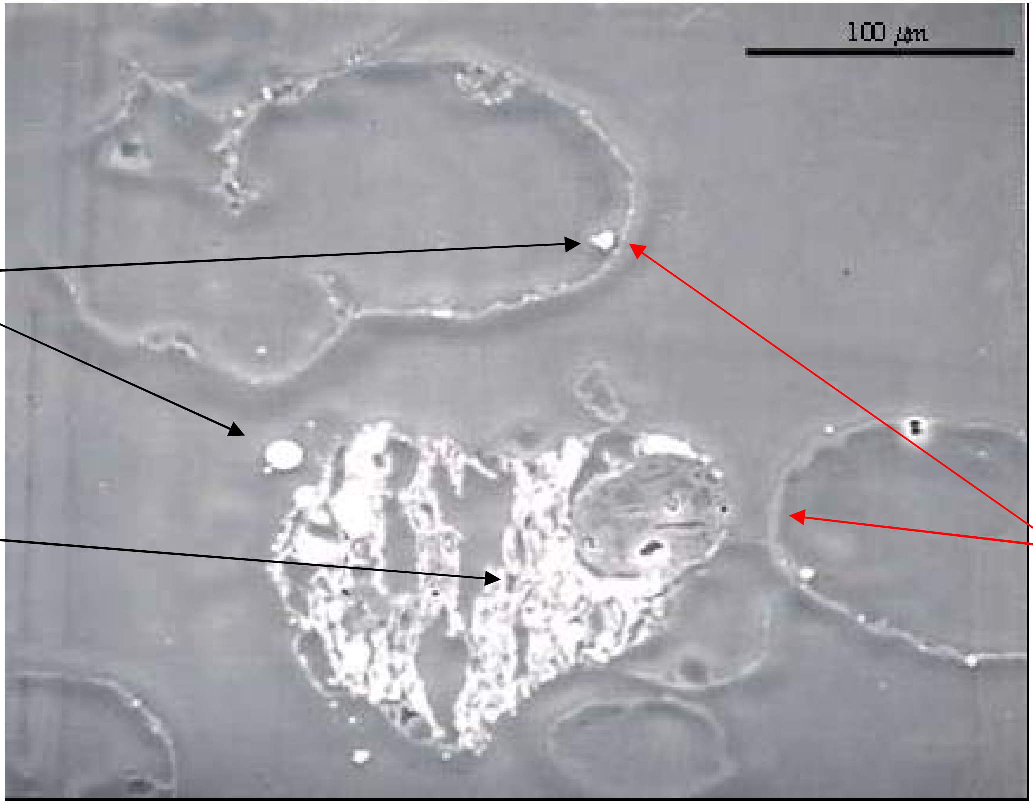
ASH FORMATION ALGORITHM



STRUCTURE EFFECTS

- Pittsburgh #8 - 10 atm

Minerals



Solid char

Wall thickness >5µm

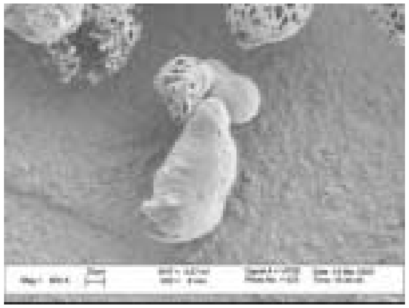
LARGE ash

Cenosphere char

Wall thickness <5 µm

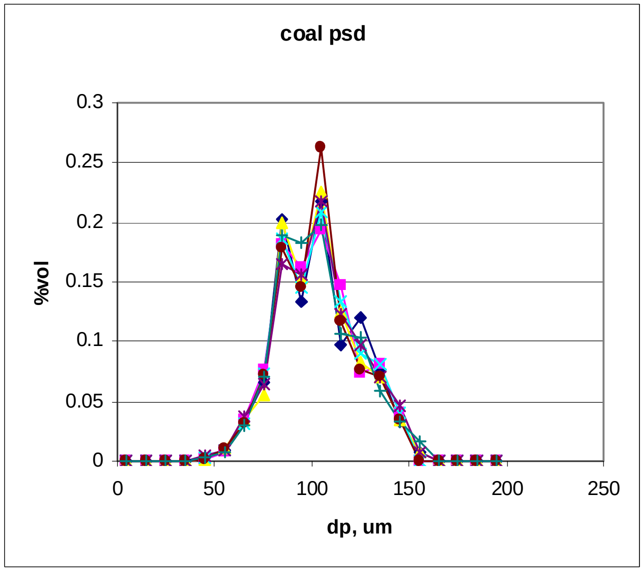
SMALL ash

Pittsburgh 8 coal particles

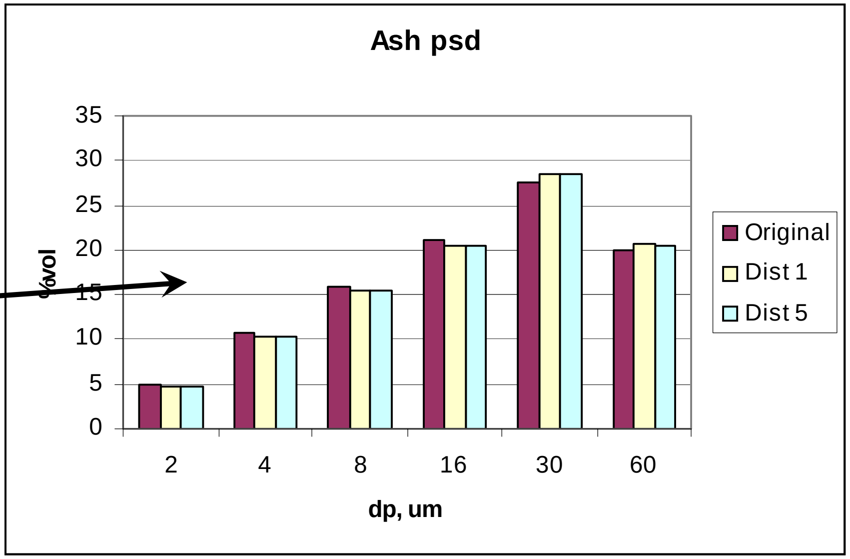


20 atm

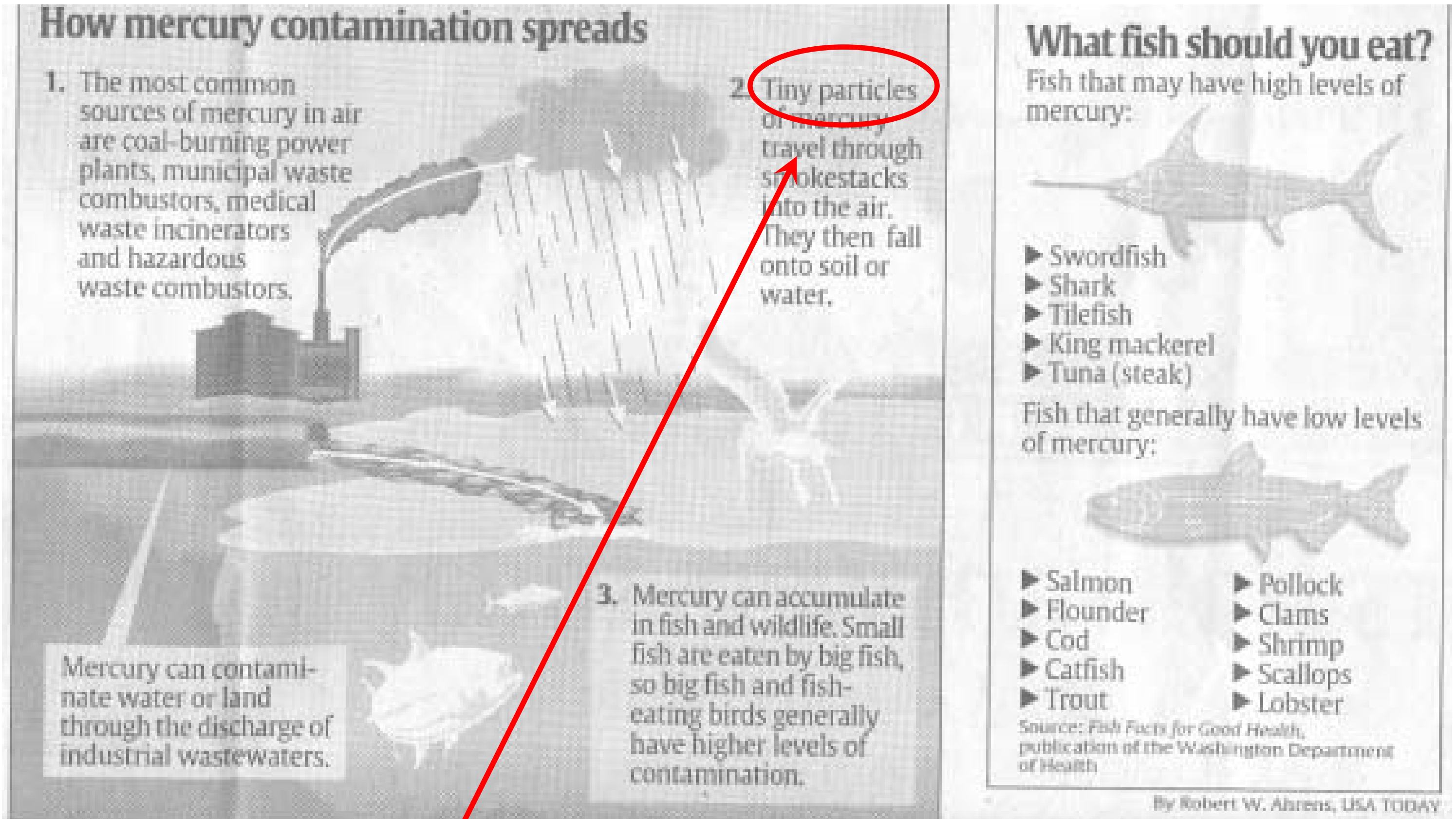
	Single particles	Dimers	Trimers	≥ Tetramers
10 atm	9%	30%	23%	38%
20 atm	15%	35%	30%	20%
30 atm	1%	17%	13%	69%



Predicted ash – little difference for dimers



Mercury in the Environment



USA Today, 11-05-02

Close… but not quite correct

Mercury ***vapor*** is important – an important distinction

The Issue with Mercury…

Mercury:

is present in coal and waste fuels

vaporizes during combustion

oxidizes only partially (important)

escapes air pollution controls if not oxidized

stays in the air for up to one year

generally deposits far from its source

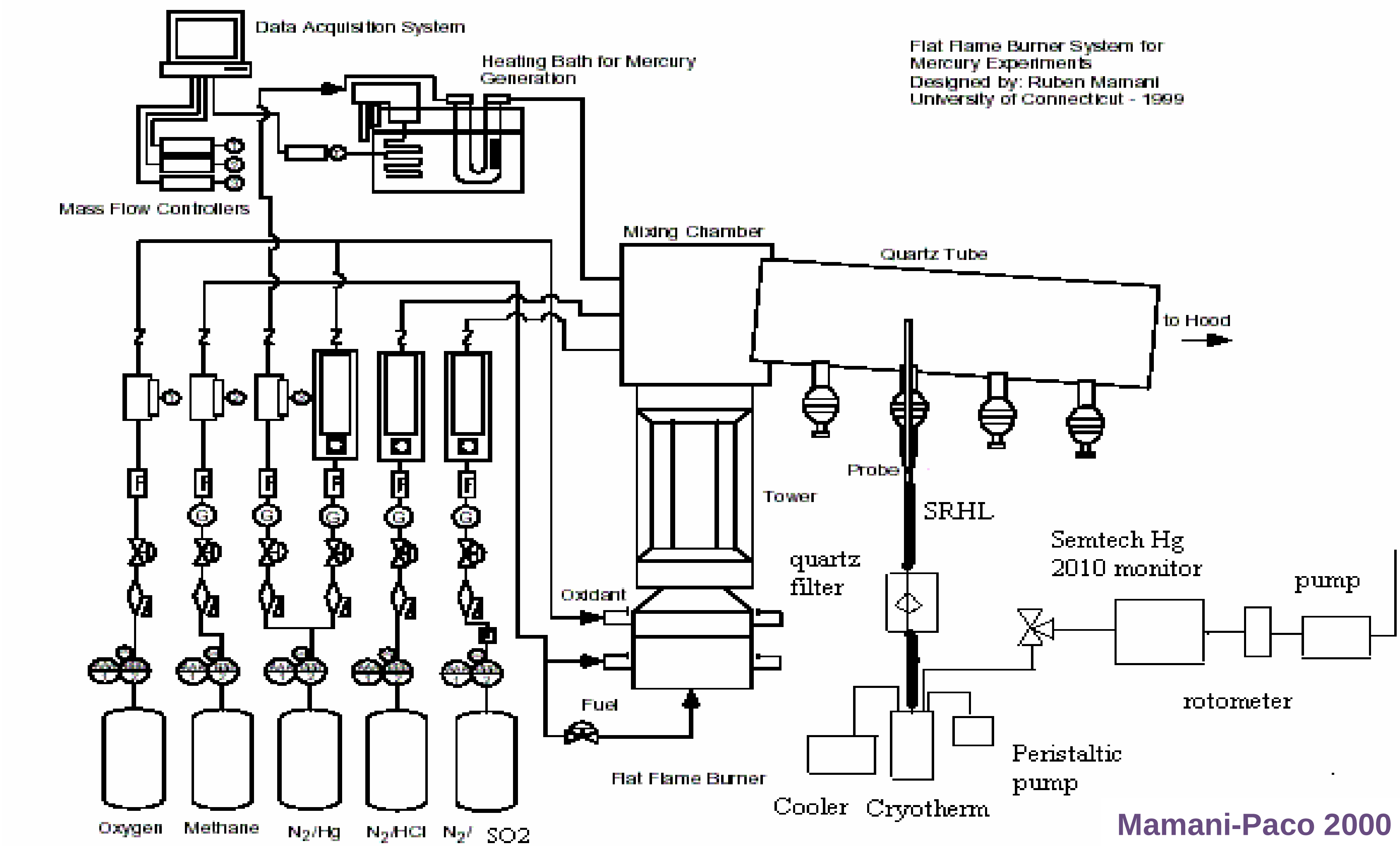
is transformed into methylmercury in the environment

bioaccumulates

To reduce hazard, must reduce emissions

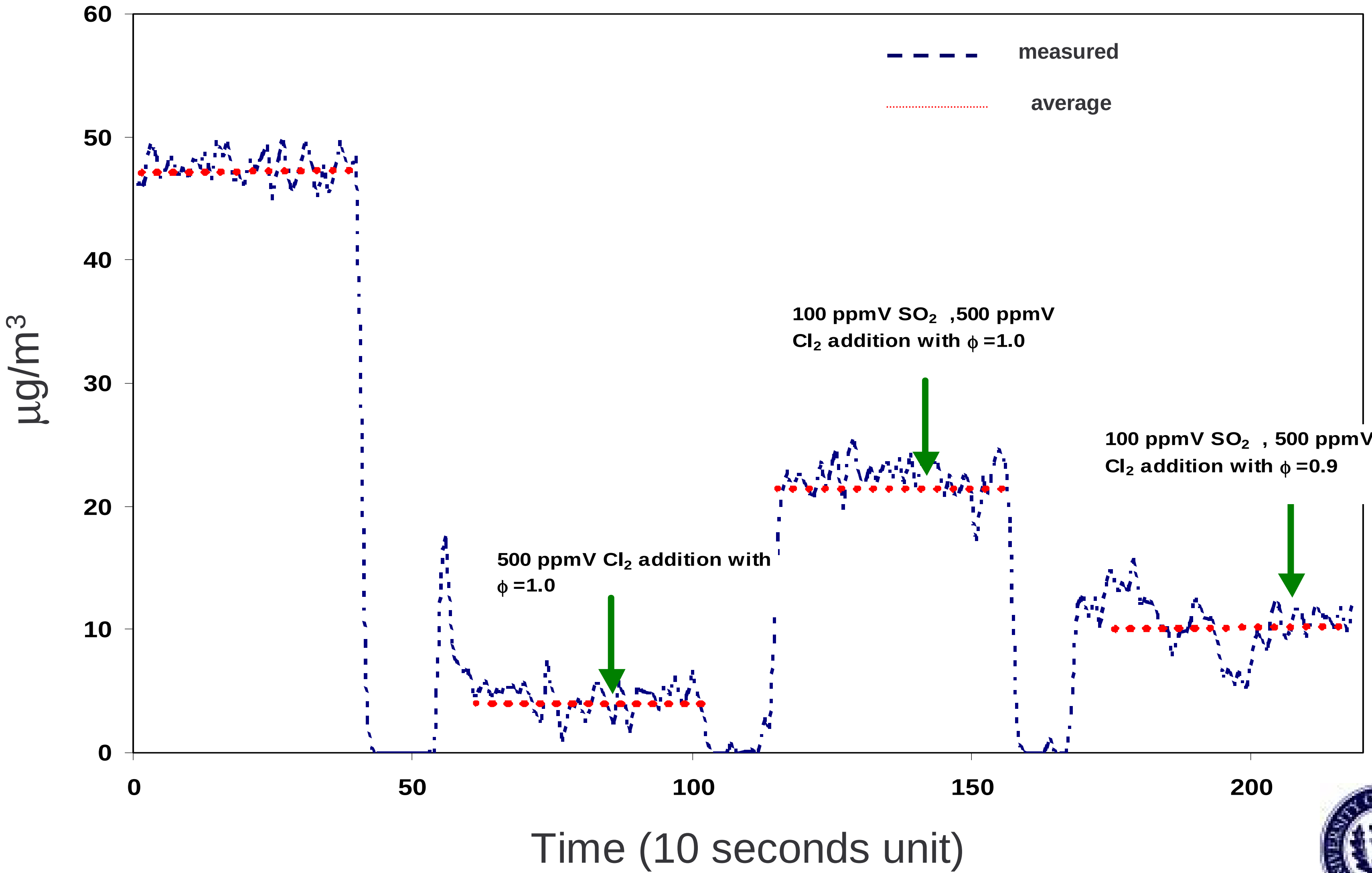
promote oxidation and capture by existing pollution controls

Mercury: Combustion Chemistry

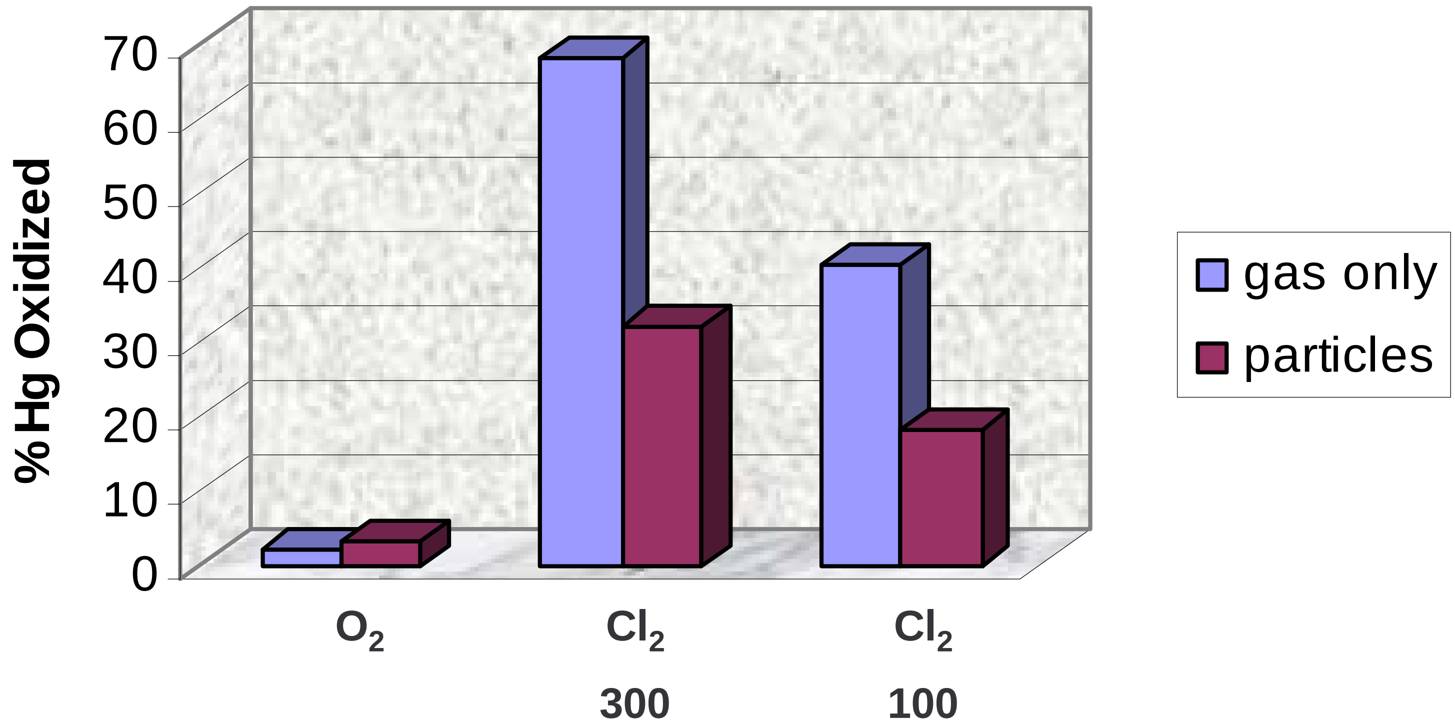


Mamani-Paco 2000

Example Result: Effects of Chlorine, Sulfur Dioxide and Oxygen



Study of Effect of Particles



Injected 5 um alumina at 5000 mg/m^3

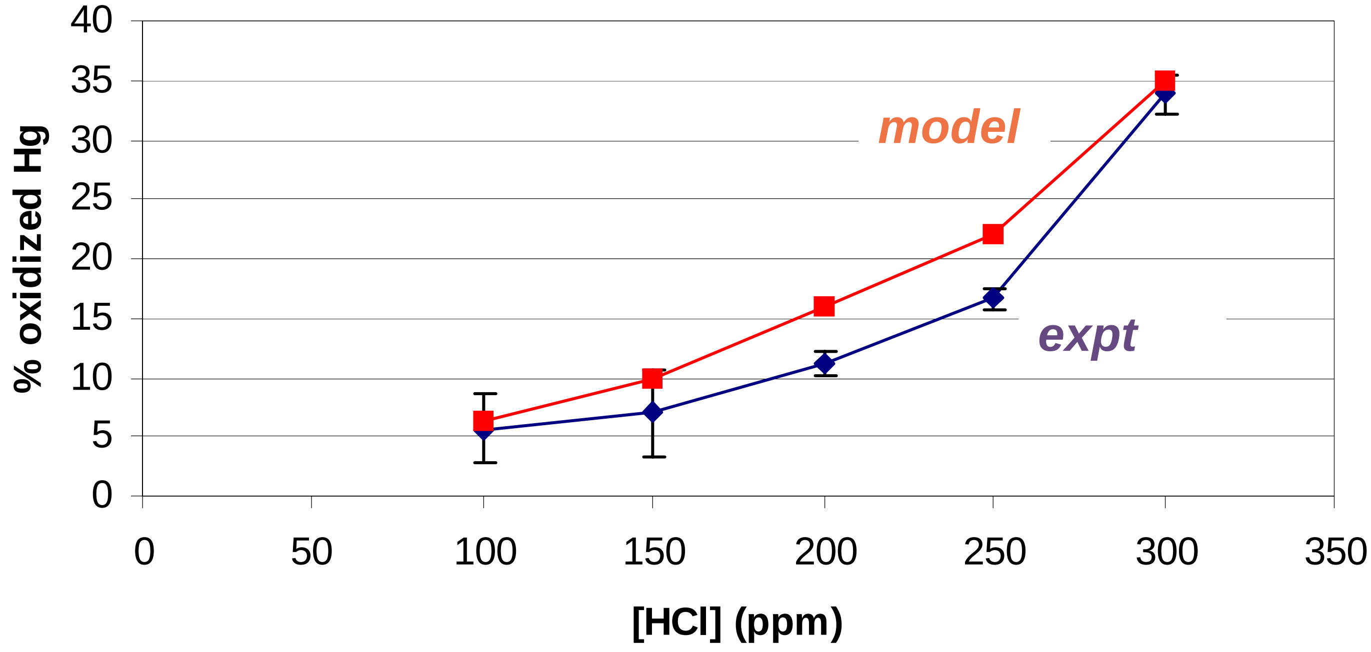
Reduces oxidation in presence of Cl_2. Increase with HCl

Proposed Oxidation Mechanism

Reaction	A (cm-mol-s)	n	E (kcal mol^{-1})
$Hg + Cl + M = HgCl + M$	9.00E+15	0.5	0
$Hg + Cl_2 = HgCl + Cl$	3.26E+10	0	22.84
$Hg + HCl = HgCl + H$	4.94E+14	0	79.30
$Hg + HOCl = HgCl + OH$	3.43E+12	0	12.79
$HgCl + Cl_2 = HgCl_2 + Cl$	2.02E+14	0	3.28
$HgCl + Cl + M = HgCl_2 + M$	1.16E+15	0.5	0
$HgCl + HCl = HgCl_2 + H$	4.94E+14	0	21.50
$HgCl + HOCl = HgCl_2 + OH$	4.27E+13	0	1.00

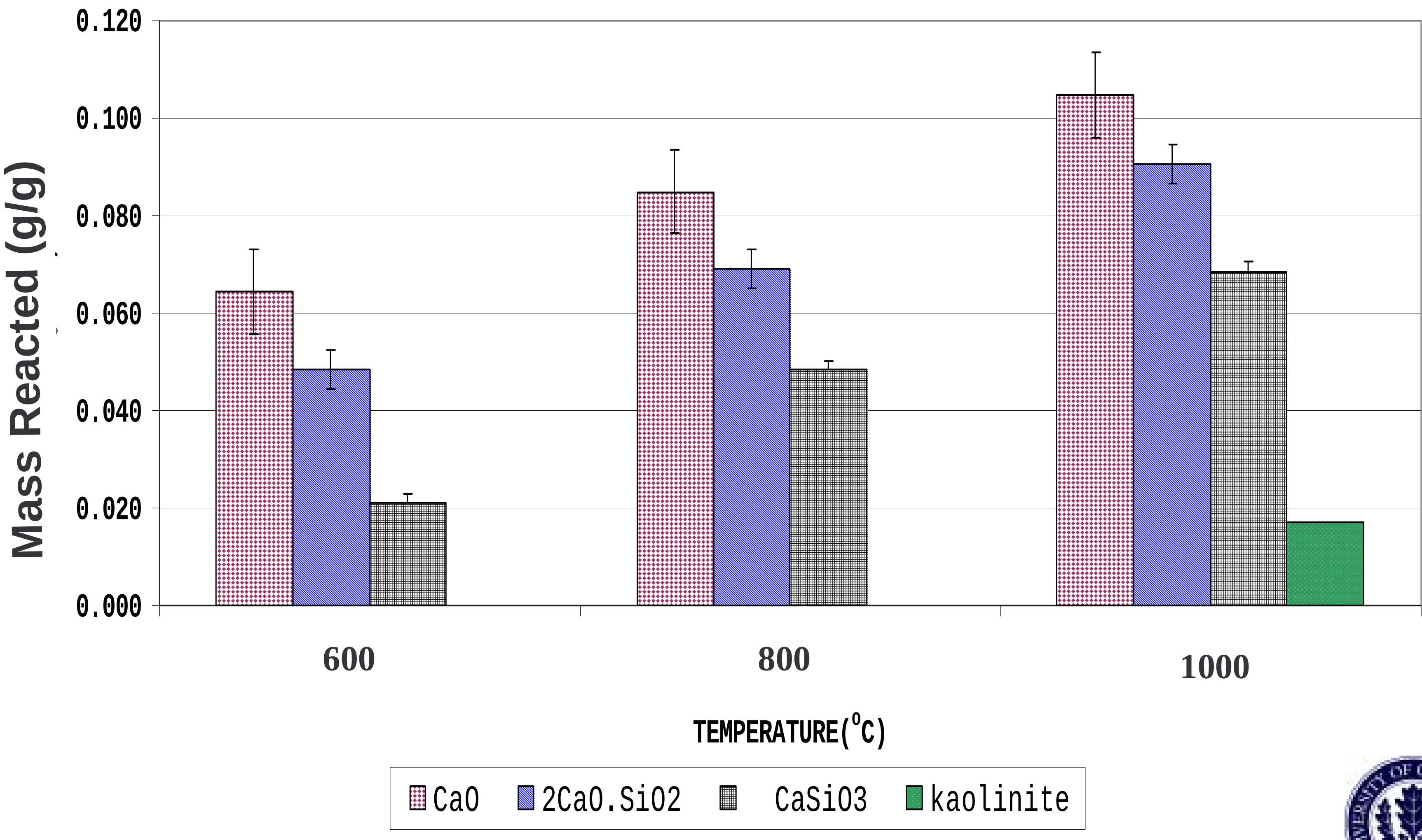
8 step sequence based on Widmer et al. (2000); Sliger et al. (2000); Niksa, Helble, and Fujiwara (2001); modified rate constants Qiu and Helble (2003)

Model Comparison

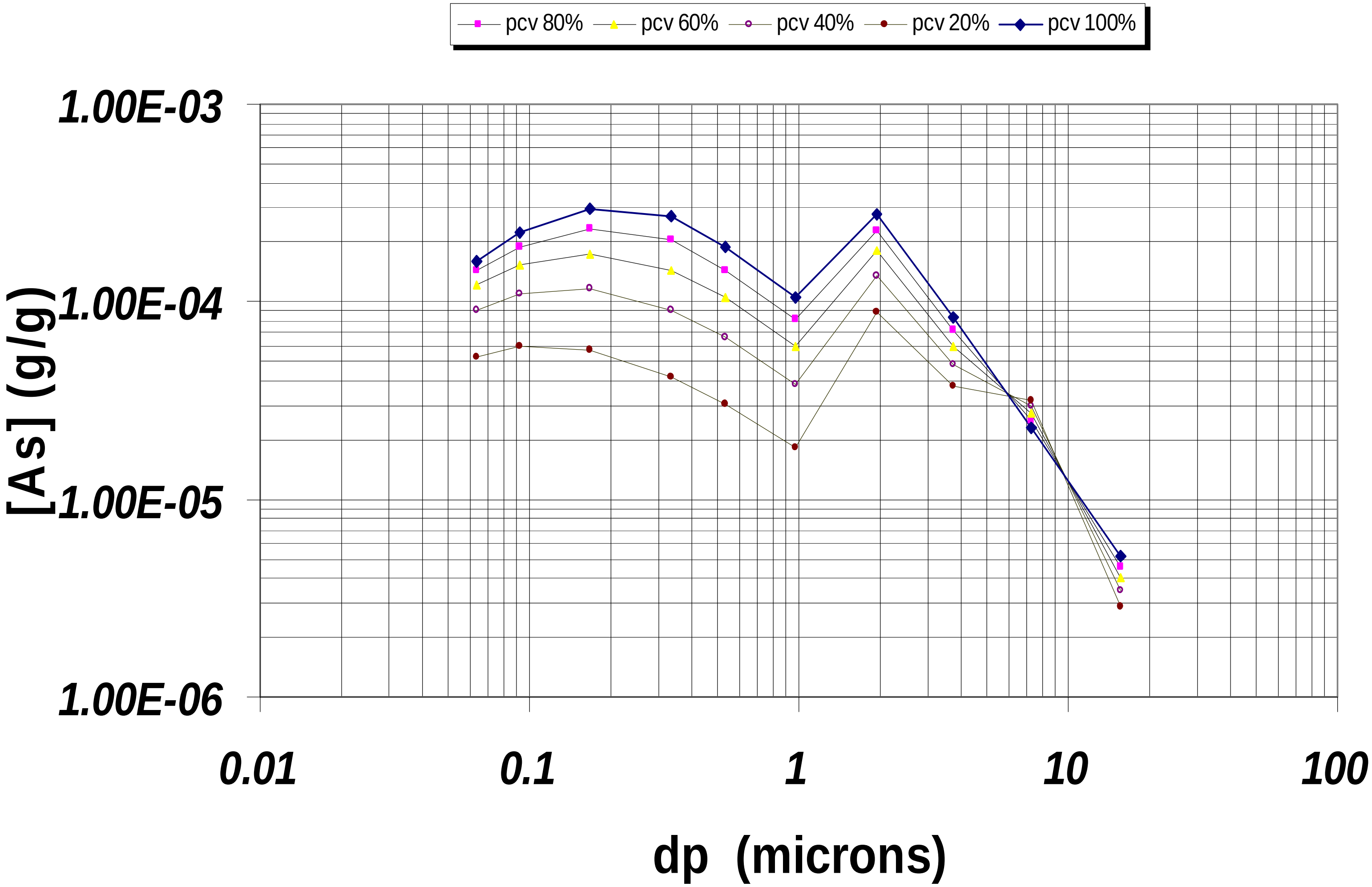


- *calculations for $\phi = 0.98$*
- *increasing O_2 to $\phi = 0.90$ increases oxidation*
- *SO_2 has little effect with HCl; NOx inhibits*
- *Cl_2 stronger oxidant; SO_2 strong inhibitor*

Reactions with Metals: As - Ca SILICATES



Modeling As Distributions with Reaction



Non-vaporized fraction associated with Ca

Non-vaporized fraction important under partial vaporization conditions

EPRI data - As

$$\eta = (PM_{in} - PM_{out})/PM_{in}$$

$$PM_{out} = (fa/H)(1-\eta)$$

$$Ei = (Ci\ PM_{out}/fa)[(1-\eta_i)/(1-\eta)]$$

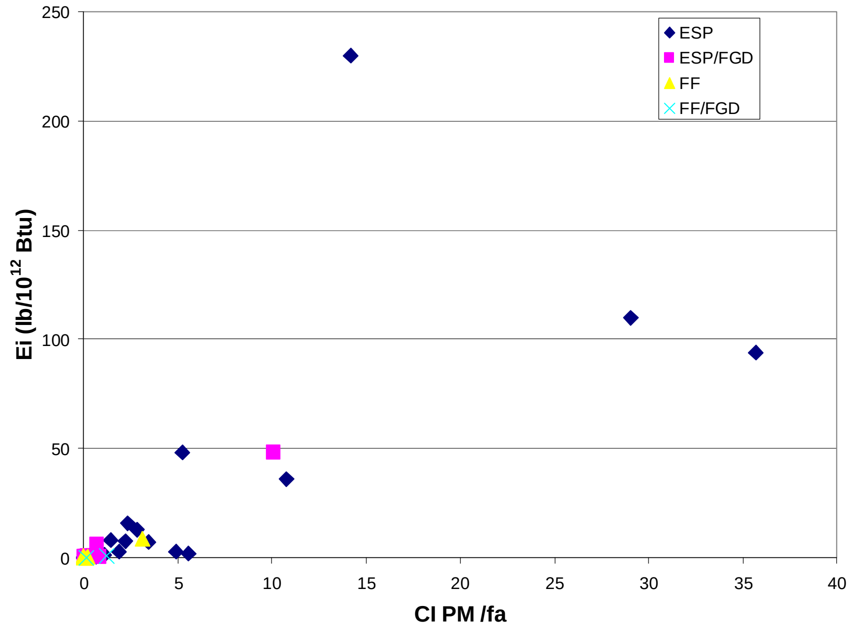
fa = ash content of coal

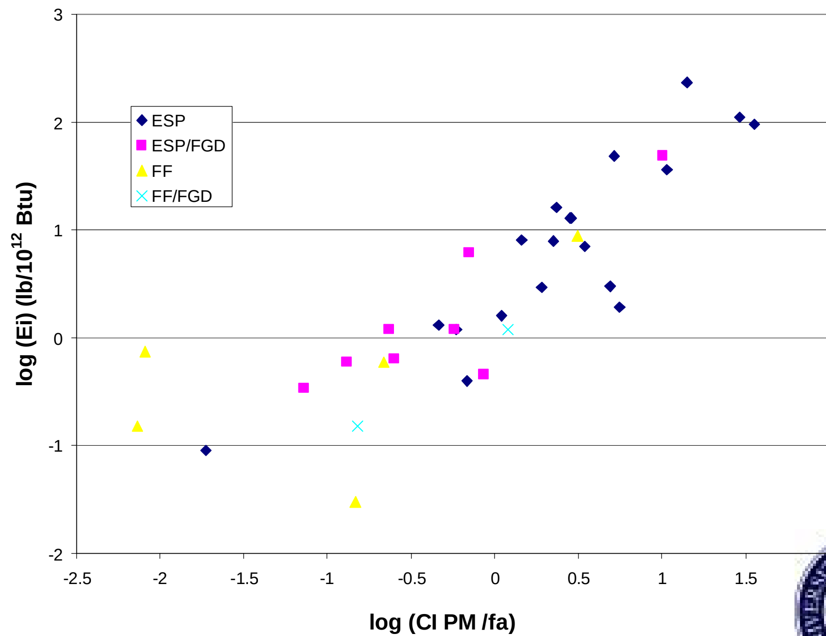
H = HHV

Ci = coal trace element content

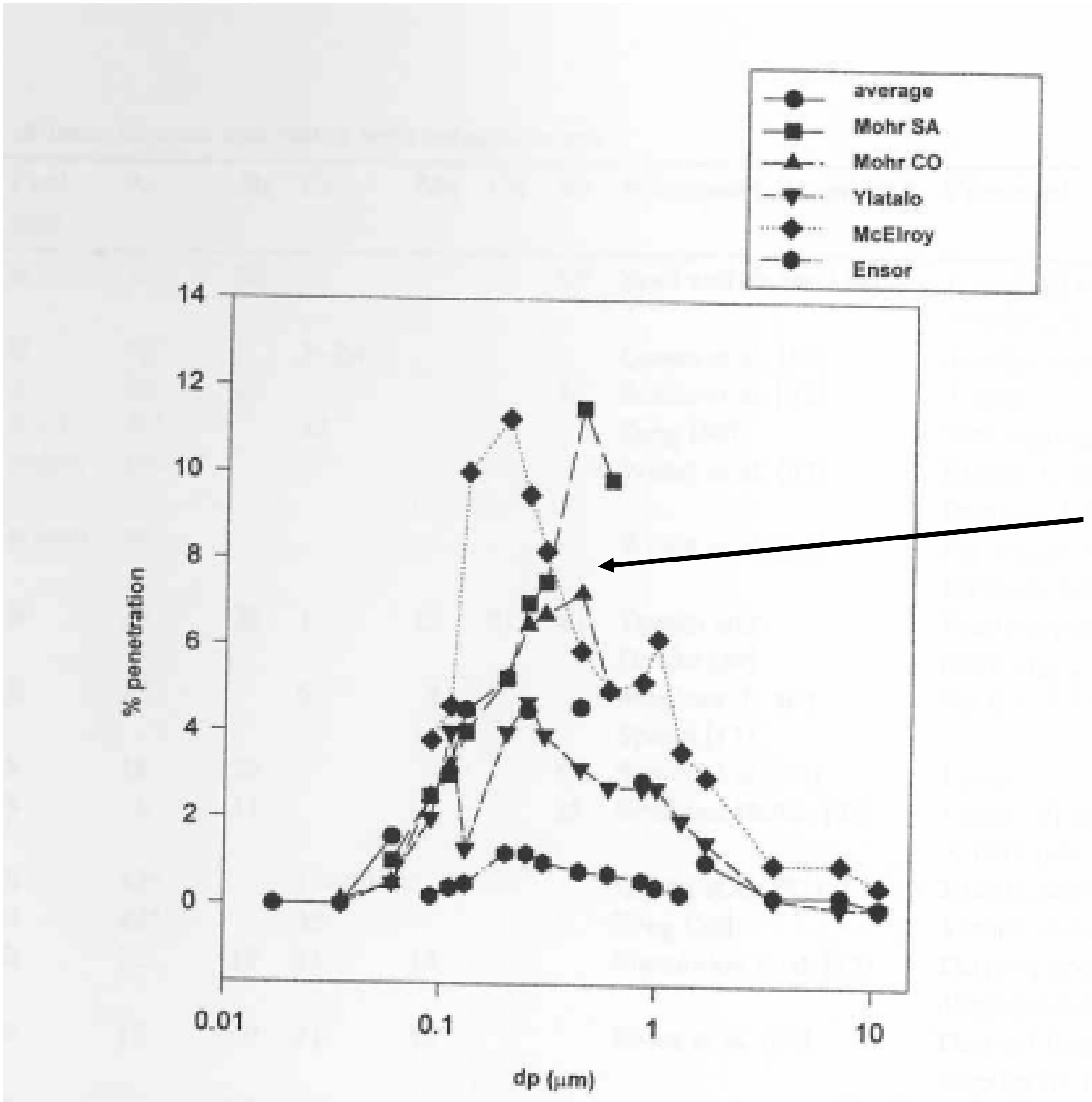
Ei = trace element emissions

greater than 100x spread in data



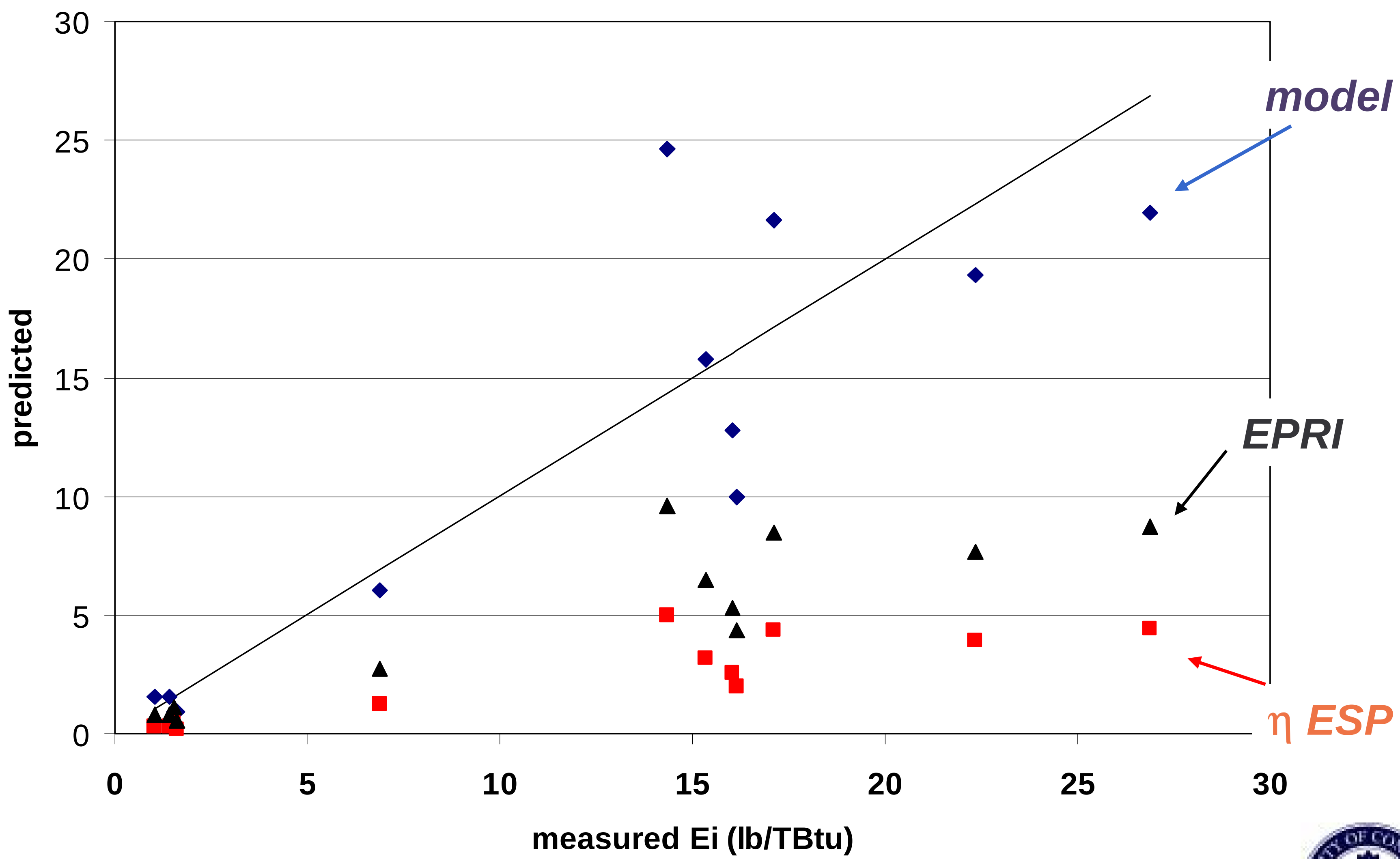


Field Data – ESP Penetration



Peak 0.1 – 1 um size range

Arsenic Emissions Prediction



25% improvement in predicted emissions

Summary of Capabiliites

Models for

- *Hg chemistry (gas phase)*
- *As, Se, other metal gas-solid reactions*
- *Emissions based on ESP penetration*
- *PM morphology (coalescence)*

Experimental programs

- *Combustion chemistry of Hg (homogeneous and heterogeneous)*
- *Trace metal gas-solid reactions*
- *PM morphology – combustion, ambient, relation to surface area*